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Single-Laboratory Evaluation of the RCRA (Resource Conservation and Recovery Act) Method for Analysis of Dioxin in Hazardous Waste

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SINGLE-LABORATORY EVALUATION OF THE RCRA METHOD FOR ANALYSIS OF DIOXIN IN HAZARDOUS WASTE

by

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16. ABSTRACT

Single-laboratory testing of RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans has been initiated on sample matrices including pottery clay soil, a Missouri soil, a fly ash, a still bottom from a chlorophenol-based herbicide production process, and an industrial process sludge. This analytical method was intended for use in the determination of chlorinated dioxin and dibenzofuran homologs with four, five, or six chlorine atoms per molecule. Revisions to the method that were found necessary for satisfactory analytical performance have been developed and have been incorporated into a revised version of the method. Single-laboratory testing of method 8280 with minor revisions demonstrated satisfactory performance for the target analytes on soil and fly ash samples. Further modification and elaboration of sample cleanup procedures were necessary for analysis of the still bottom and industrial sludge samples.

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FOREWORD

Largely as a result of finding trace levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) as a contaminant in commercial preparations of chlorophenol-based herbicides, the U.S. Environmental Protection Agency (EPA) initiated (in 1973) monitoring efforts for 2,3,7,8-TCDD in environmental samples. Later findings of contamination by 2,3,7,8-TCDD in soil samples from Niagara Falls, New York, and numerous sites in Missouri led to extensive sampling and analysis efforts. It is now known that many, if not all, of the 75 possible chlorinated dioxins and 135 structurally related chlorinated dibenzofurans possess relatively high toxicity to man and certain animal species. Most of the available acute and chronic toxicological data for the chlorinated dioxins and dibenzofurans is based upon the 2,3,7,8-TCDD isomer. In certain animal species (notably, the guinea pig), extraordinarily low doses may be lethal. As such, these compounds are considered to be the most potent man-made toxicants. Exposure to these compounds has been observed to produce a wide range of systemic effects including hepatic disorders, carcinoma, and teratogenicity in certain animal species, although the major documented effect upon humans has been chloracne.

The EPA has determined[1] that enhanced toxicities are likely to be observed with samples containing tetra-, penta-, and hexa-chlorinated dioxins and dibenzofurans. In 1983,[2] the EPA proposed a ruling affecting disposal of hazardous wastes containing tetra-, penta-, and hexa-chlorinated dioxins and dibenzofurans. These wastes would be managed under the Resource Conservation and Recovery Act (RCRA) and would be analyzed for the target chlorinated dioxins and dibenzofurans using an analytical method which was included as an Appendix to the proposed rule (method 8280).

In order to manage these wastes effectively, it is necessary to obtain data regarding the performance of the method as proposed in the Federal Register for the analysis of dioxin- and furan-containing wastes. This study was intended to determine and elaborate any changes needed for satisfactory method performance and to provide method performance data after revisions had been made. Hazardous waste sample types/matrices which have been subjected to analysis under this method include soils, a carbonaceous material (fly ash), a chlorophenol production still bottom, and an industrial sludge.

This report summarizes results obtained under a single-laboratory evaluation of RCRA method 8280. Method performance results are presented; and needed revisions are included and supported with data and rationale. This revised method has been shown to perform well on several sample types.

ABSTRACT

Single-laboratory testing of RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans has been initiated on sample matrices including pottery clay soil, a Missouri soil, a fly ash, a still bottom from a chlorophenol-based herbicide production process, and an industrial process sludge. This analytical method was intended for use in the determination of chlorinated dioxin and dibenzofuran homologs with four, five, or six chlorine atoms per molecule. Revisions to the method that were found necessary for satisfactory analytical performance have been developed and have been incorporated into a revised version of the method.

Single-laboratory testing of method 8280 with minor revisions demonstrated satisfactory performance for the target analytes on soil and fly ash samples. Further modification and elaboration of sample cleanup procedures were necessary for analysis of the still bottom and industrial sludge samples.

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LIST OF ABBREVIATIONS

CLP	- Contract Laboratory Program
DL	- detection limit
GC/EC	- gas chromatography/electron capture detection
GC/MS	- gas chromatography/mass spectrometry
HpCDD	- heptachlorodibenzo-p-dioxin (hepta-CDD)
HpCDF	- heptachlorodibenzofuran (hepta-CDF)
HPLC	- high performance liquid chromatography
HRGC	- high resolution gas chromatography
HxCDD	- hexachlorodibenzo-p-dioxin (hexa-CDD)
HxCDF	- hexachlorodibenzofuran (hexa-CDF)
LRMS (or MS)	- low resolution mass spectrometry
MID	- multiple ion detection
OCDD	- octachlorodibenzo-p-dioxin
OCDF	- octachlorodibenzofuran
PCDD	- polychlorodibenzo-p-dioxin
PCDF	- polychlorodibenzofuran
PeCDD	- pentachlorodibenzo-p-dioxin (penta-CDD)
PeCDF	- pentachlorodibenzofuran (penta-CDF)
ppb	- parts per billion
ppt	- parts per trillion
RIC	- reconstructed ion chromatogram
TCDD	- tetrachlorodibenzo-p-dioxin (tetra-CDD); often used for the 2,3,7,8-TCDD isomer
TCDF	- tetrachlorodibenzofuran (tetra-CDF)
m/z	- mass to charge ratio

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SECTION 1

INTRODUCTION

RCRA Method 8280 as initially proposed for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans consists of four major sections: (1) extraction of the analytes from the sample· (2) "open" column chromatographic cleanup with alumina using a methylene chloride/hexane eluent; (3) optional HPLC cleanup; and (4) analysis by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). To test the method efficiently and to develop appropriate modifications with minimal redundancy, each section of the method was tested separately. Initial tests were performed on a simple sample matrix (pottery clay soil) and on standard solutions. Only after adequate method-performance data was collected on such materials was the analysis of more complex samples investigated. The first step to be elaborated was the measurement technique. High resolution gas chromatography with mass spectrometry detection (HRGC/MS) and with electron capture detection (HRGC/EC) were both tested, using guidelines from the published RCRA method. A portion of this aspect of the study included evaluating several types of GC columns as a test of resolution and stability. Given the requirements of the MS detector, the cleanup steps were then studied in detail and appropriate modifications were investigated and documented. Additional evaluation of the method involved a systematic investigation of the other major sections. This procedure allowed for a separate description of each section of the method to document any recommended modifications.

SECTION 2

CONCLUSIONS

The major revisions which were made to the published method include: (1) the addition of a carbon column cleanup procedure to eliminate closely related chemical species; (2) modification of the alumina column elution pattern so that all desired analytes eluted in a single fraction, with the bulk of the analytical interferences removed; (3) expansion of the extraction step so that wet samples could be accommodated; (4) development of HPLC procedures that could be performed reproducibly and efficiently; and (5) expansion of the list of analytes to include a hepta- and the octa-chloro isomer of dibenzo-p-dioxin.

Performance of the revised method was investigated by precision and accuracy determinations, by recovery of spiked analytes and isotopically-labeled standards, and by using two independent teams of analysts. Effects of certain experimental parameters, such as GC column type (coating) and alumina activation level, are also noted in this report.

After incorporating necessary revisions, satisfactory method performance has been demonstrated on RCRA type samples. Performance of the method on relatively complex matrices, such as sludges, still bottoms, and fly ash, has been determined, and precision and accuracy data is reported. Estimates of detection limits in these matrices are also reported.

SECTION 3

RECOMMENDATIONS

The revised protocol has been single laboratory validated for selected PCDD's and PCDF's in five different types of samples typical of those expected to be analyzed under RCRA monitoring requirements. An interlaboratory comparison test using all available PCDD and PCDF analytes in selected matrices should be the next laboratory test of the procedure.

Expansion of the analysis to other PCDD's and PCDF's is recommended as standards become available. Analysis of new sample matrix types will allow for further refinement of the protocol.

SECTION 4

EXTRACTION METHOD DEVELOPMENT AND REVISIONS

A pottery clay sample was selected as a model matrix for determining the extraction efficiency obtained following the recommended method. A 50 ng spike of 2,3,7,8-TCDD was added, and extraction was performed as specified in the unrevised method. This experiment was performed in triplicate on clay and fly ash samples as shown in Table 1. The fly ash matrix is discussed in more detail in Section 9. As can be seen, even on such a simple system, extraction performance is poor. Therefore, a modified extraction solvent system and procedure were developed. This modified procedure adds methanol and sodium sulfate to the petroleum ether solvent specified in the RCRA method and uses a Kuderna-Danish concentration technique. Following these modifications, these experiments were repeated and the results are shown in Table 2; performance is improved on both dry and wet samples. As shown in the pottery clay and Missouri soil sections of this report, the revised extraction procedure resulted in satisfactory overall method performance (e.g., dioxin-surrogate spike recovery values) and is recommended for inclusion in the revised method.

TABLE 1. PERFORMANCE OF UNREVISED* METHOD 8280

Analyte	Matrix	Percent Recovery Extraction**	Percent Recovery Cleanup	Total Calculated % Recovery
2,3,7,8-TCDD	clay	44	42	18
	fly ash	90	42	38
1,2,3,4-TCDD	clay	44	15	7
	fly ash	90	15	14
1,2,3,4,7-PeCDD	clay	44	0	0
	fly ash	90	0	0
1,2,3,4,7,8-HxCDD	clay	44	11	5
	fly ash	90	11	10
2,3,7,8-TCDF	clay	44	48	21
	fly ash	90	48	43

*Specific ions required for these analytes were monitored.
**Extraction recoveries estimated for other analytes are based upon actual recovery of $^{13}C_{12}$-2,3,7,8-TCDD.

TABLE 2. SOIL EXTRACTION METHOD DEVELOPMENT: RCRA METHOD AS PUBLISHED VERSUS REVISED EXTRACTION PROCEDURE

Sample ID	Weight Clay	Weight Water	Method	Percent Recovery of Spiked 2,3,7,8-TCDD
RCRA-D1	10.0 g	--	8280*	37.5%
RCRA-D2	10.0 g	--	8280*	55.0%
RCRA-D3	10.0 g	--	8280*	38.7%
RCRA-W1	5.0 g	5.0 g	8280*	ND
RCRA-W2	5.0 g	5.0 g	8280*	ND
RCRA-W3	5.0 g	5.0 g	8280*	ND
D-1	10.0 g	--	Rev. 8280**	96%
D-2	10.0 g	--	Rev. 8280**	72%
W-1	5.0 g	5.0 g	Rev. 8280**	68%
W-2	5.0 g	5.0 g	Rev. 8280**	96%

*RCRA Method 8280 was used without any drying of sample.
**Revised Method 8280 as presented in this report, Appendix A.
ND = None detected; TCDD spiked at 50 ng/10 g clay; estimated detection limit 75 pg.

SECTION 5

DEVELOPMENT OF ALUMINA CLEANUP PROCEDURE

Experimental conditions for elution of the analytes from the "open" alumina chromatographic column were determined to be crucial to method performance. Using conditions as specified in the Federal Register (40 CFR 65: 14514ff, April 4, 1983), the elution profile shown in Table 3 was obtained. This profile was unsatisfactory because many analytes of interest eluted in the 20 percent CH_2Cl_2/hexane fraction that was to be discarded. Furthermore, over half of the 2,3,7,8-TCDD failed to elute, until an added step using 60 percent CH_2Cl_2 in hexane was performed. Changing the solvent eluent to 5 percent, 20 percent, and 60 percent CH_2Cl_2 in hexane provided complete elution of the 2,3,7,8-TCDD, but many of the target analytes also eluted in the 20 percent fraction, as shown in Table 4. Use of 10 percent and 60 percent CH_2Cl_2 in hexane eluent caused all analytes of interest to appear in the 60 percent fraction, as shown in Table 5. An elution volume of 15 mL for each fraction was consistently used.

Because use of basic materials might cause formation of chlorinated dioxins and dibenzofurans when chlorophenols and hydroxydiphenylethers are present,[4] it is considered preferable to use neutral alumina. Further, it would be convenient and would eliminate a potential source of contamination if the furnace-drying required of the basic alumina, as specified in the unrevised method, could be avoided. Therefore, readily available Woelm Super 1 alumina was tested. This material provided elution patterns as shown in Tables 6 and 7. Since the Woelm Super 1 alumina was more convenient to use, avoided exposure of the sample to a basic substrate, and provided fully satisfactory elution patterns, it was specified for use in the revised method. To demonstrate the effect of deactivating Woelm Super 1 alumina by addition of water (via wet solvents, wet sample, or intentional deactivation), elution profiles were determined on Woelm Activity Grade I (1 percent added water) and with Woelm Activity Grade II (4 percent added water). These profiles are presented in Tables 8 and 9, respectively.

Results presented in Tables 3 through 9 show that the activation level of the alumina chosen is crucial to satisfactory method performance for two reasons. First, loss of a percentage of an analyte degrades the method detection limit, and second, recoveries of different analytes are affected to quite different extents, rendering recovery values obtained on one isotopically-labeled analyte meaningless for another analyte. It is also obvious that if the presence of very small amounts of water affects elution patterns greatly, controls must be exerted to ensure that alumina used is of reproducible and known activity level (percent water). Note: When the revised procedure is used, the bulk of potential interferants elute in the 5 percent, 10 percent, and/or 20 percent methylene chloride/hexane fraction in all cases.

TABLE 3. ELUTION OF ANALYTES FROM BASIC ALUMINA
(PER UNREVISED RCRA METHOD 8280)*

Analyte	Percent CH_2Cl_2 in Hexane (v/v)			
	3%	20%	50%	60%
2,3,7,8-TCDF		52	48	
1,2,3,4-TCDD		85	15	
2,3,7,8-TCDD			42	58
1,2,3,4,7-PeCDD		100		
1,2,3,4,7,8-HxCDD		89	11	
1,2,3,4,6,7,8-HpCDD		25	75	
OCDD			100	

*Amount of analyte in eluate expressed in percent of total recovered from column.

TABLE 4. ELUTION OF ANALYTES FROM BASIC ALUMINA*

Analyte	Percent CH_2Cl_2 in Hexane (v/v)		
	5%	20%	60%
2,3,7,8-TCDF		9	91
1,2,3,4-TCDD		100	
2,3,7,8-TCDD			100
1,2,3,4,7-PeCDD		90	10
1,2,3,4,7,8-HxCDD		58	42
1,2,3,4,6,7,8-HpCDD		8	92
OCDD			100

*Amount of analyte in eluate expressed in percent of total recovered from column.

TABLE 5. ELUTION OF ANALYTES FROM BASIC ALUMINA*

Analyte	Percent CH_2Cl_2 in Hexane (v/v)	
	10%	60%
2,3,7,8-TCDF		100
1,2,3,4-TCDD		100
2,3,7,8-TCDD		100
1,2,3,4,7-PeCDD		100
1,2,3,4,7,8-HxCDD		100
1,2,3,4,6,7,8-HpCDD		100
OCDD		100

*Amount of analyte in eluate expressed in percent of total recovered from column.

TABLE 6. ELUTION OF ANALYTES FROM NEUTRAL ALUMINA* (WOELM SUPER 1)

Analyte	Percent CH_2Cl_2 in Hexane (v/v)		
	5%	20%	60%
2,3,7,8-TCDF			100
1,2,3,4-TCDD		95	5
2,3,7,8-TCDD			100
1,2,3,4,7-PeCDD		94	6
1,2,3,4,7,8-HxCDD		80	20
1,2,3,4,6,7,8-HpCDD		29	71
OCDD		4	96

*Amount of analyte in eluate expressed in percent of total recovered from column.

TABLE 7. ELUTION OF ANALYTES FROM NEUTRAL ALUMINA (WOELM SUPER 1)

Analyte	Percent CH_2Cl_2 in Hexane (v/v) 10%	60%
2,3,7,8-TCDF		100
1,2,3,4-TCDD		100
2,3,7,8-TCDD		100
1,2,3,4,7-PeCDD		100
1,2,3,4,7,8-HxCDD		100
1,2,3,4,6,7,8-HpCDD		100
OCDD		100

*Amount of analyte in eluate expressed in percent of total recovered from column.

TABLE 8. ELUTION OF ANALYTES FROM WOELM SUPER 1 NEUTRAL ALUMINA DEACTIVATED WITH 1 PERCENT WATER*

Analyte	Percent CH_2Cl_2 in Hexane (v/v) 10%	60%
2,3,7,8-TCDF	2	98
1,2,3,4-TCDD	59.5	40.5
2,3,7,8-TCDD		100
1,2,3,4,7-PeCDD	64	36
1,2,3,4,7,8-HxCDD	74.5	25.5
1,2,3,4,6,7,8-HpCDD	46	54

*Amount of analyte in eluate expressed in percent of total recovered from column.

TABLE 9. ELUTION OF ANALYTES FROM WOELM SUPER 1 NEUTRAL ALUMINA DEACTIVATED WITH 4 PERCENT WATER*

Analyte	Percent CH_2Cl_2 in Hexane (v/v)	
	10%	60%
2,3,7,8-TCDF	96	4
1,2,3,4-TCDD	97.5	2.5
2,3,7,8-TCDD	85	15
1,2,3,4,7-PeCDD	97.5	2.5
1,2,3,4,7,8-HxCDD	100	
1,2,3,4,6,7,8-HpCDD	99	1

*Amount of analyte in eluate expressed in percent of total recovered from column.

Initial experiments were performed by preparing spiking solutions of selected analytes (50 ng each) and applying them directly to the top of the column. Eluates were analyzed by HRGC/EC and by HRGC/MS to determine which eluate fraction(s) contained the compounds spiked onto the column. These elution experiments were performed with the analytes spiked at 50 ng each, plus 2.5 µg each of Aroclor 1016, Aroclor 1254, Aroclor 1260, pentachlorophenol, dibenzofuran, Silvex 2,4,5-T, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, and p,p'-DDE in the spiking solution. Sample chromatograms demonstrating the effect of this cleanup procedure are presented in Figures 1 through 3. The bulk of the interferences elute in the 10 percent CH_2Cl_2/hexane fraction, as shown in Figure 2. These chromatograms were obtained by HPLC/UV using methanol solvent (isocratic).

Note that while the elution percentages in Tables 3 through 9 represent percent of total target analyte recovered from the column, all columns yielded essentially quantitative recoveries.

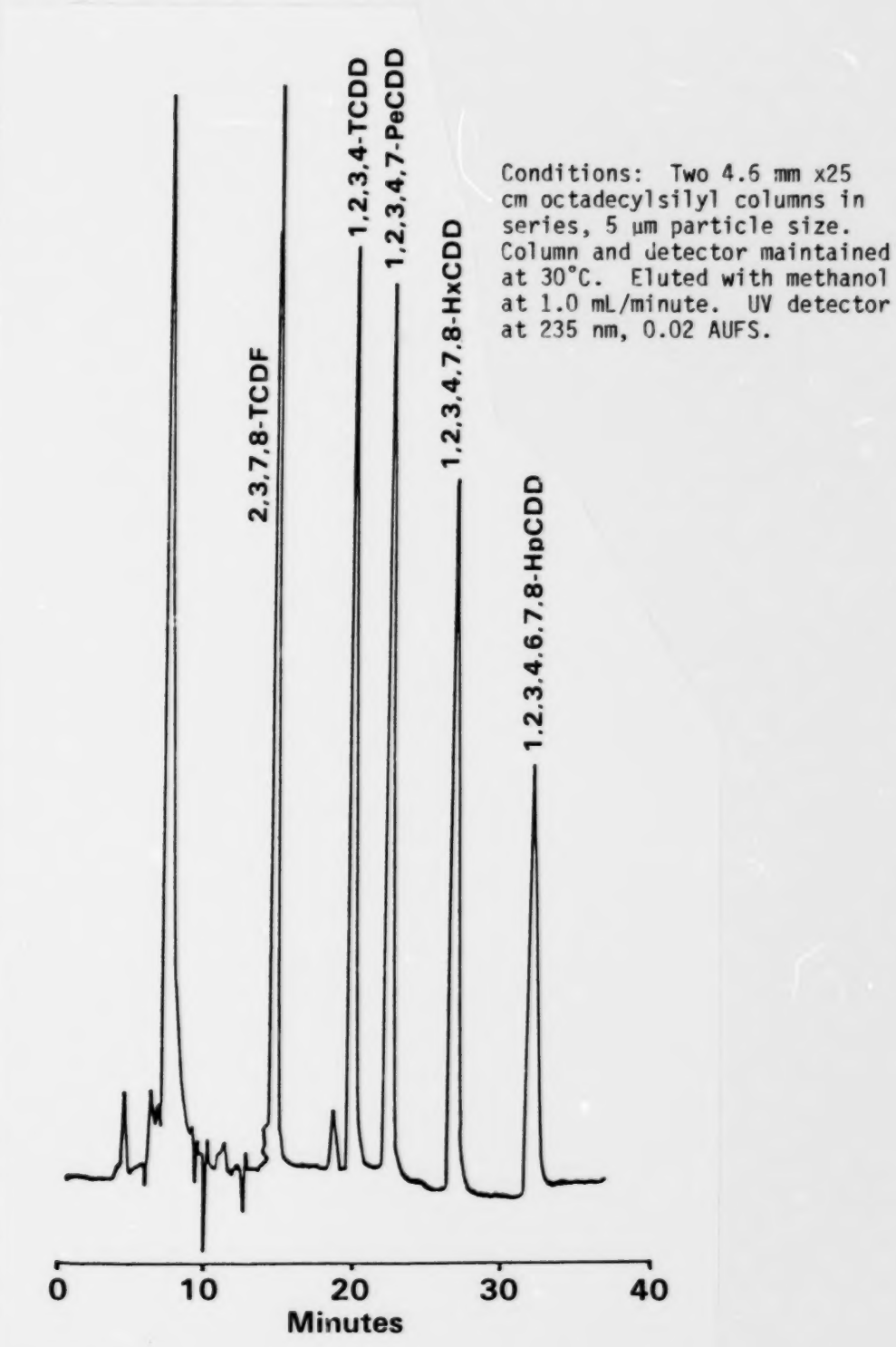

Figure 1. HPLC analysis of analyte standard mixture.

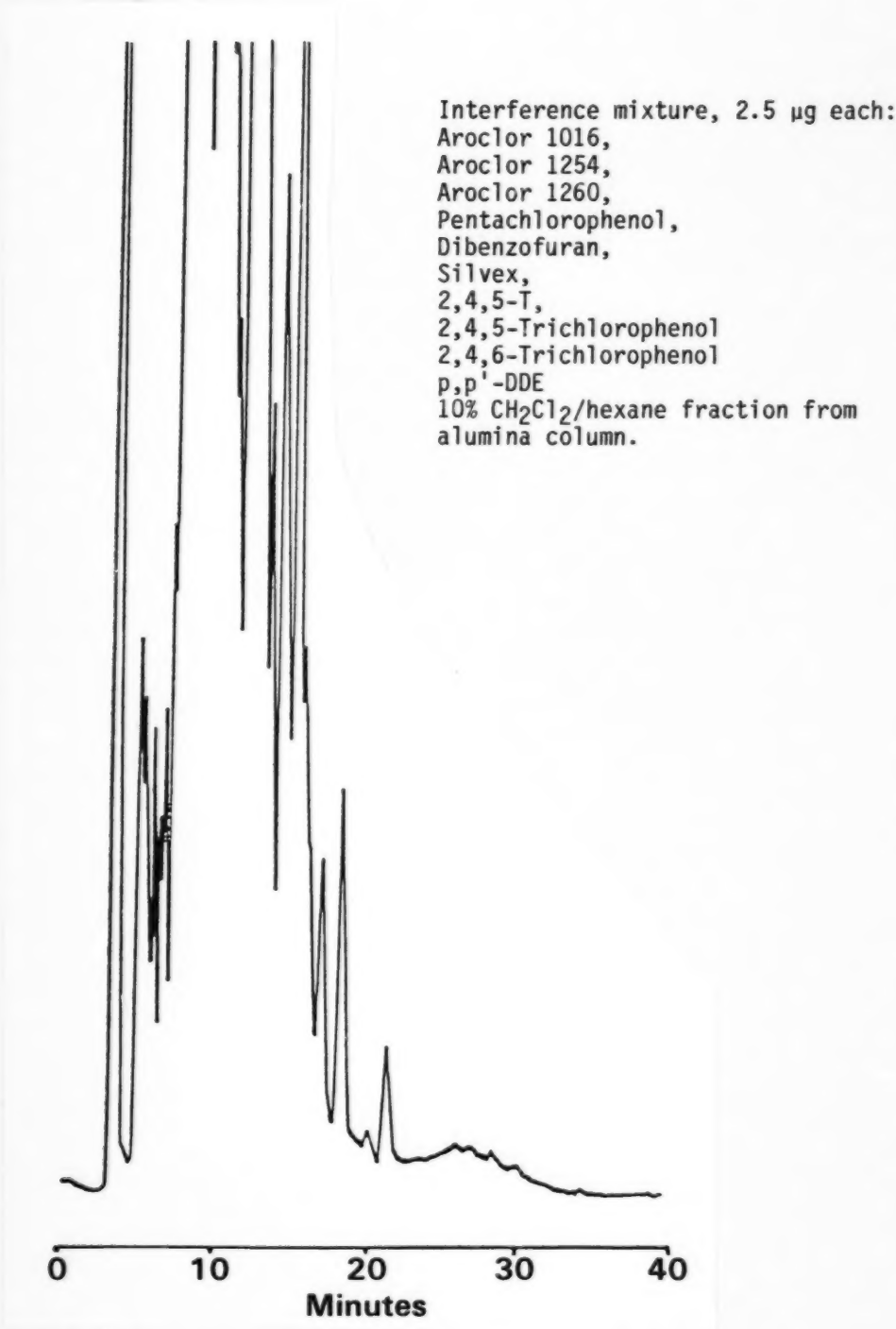

Figure 2. HPLC analysis of analyte standard mixture spiked with interference mixture.

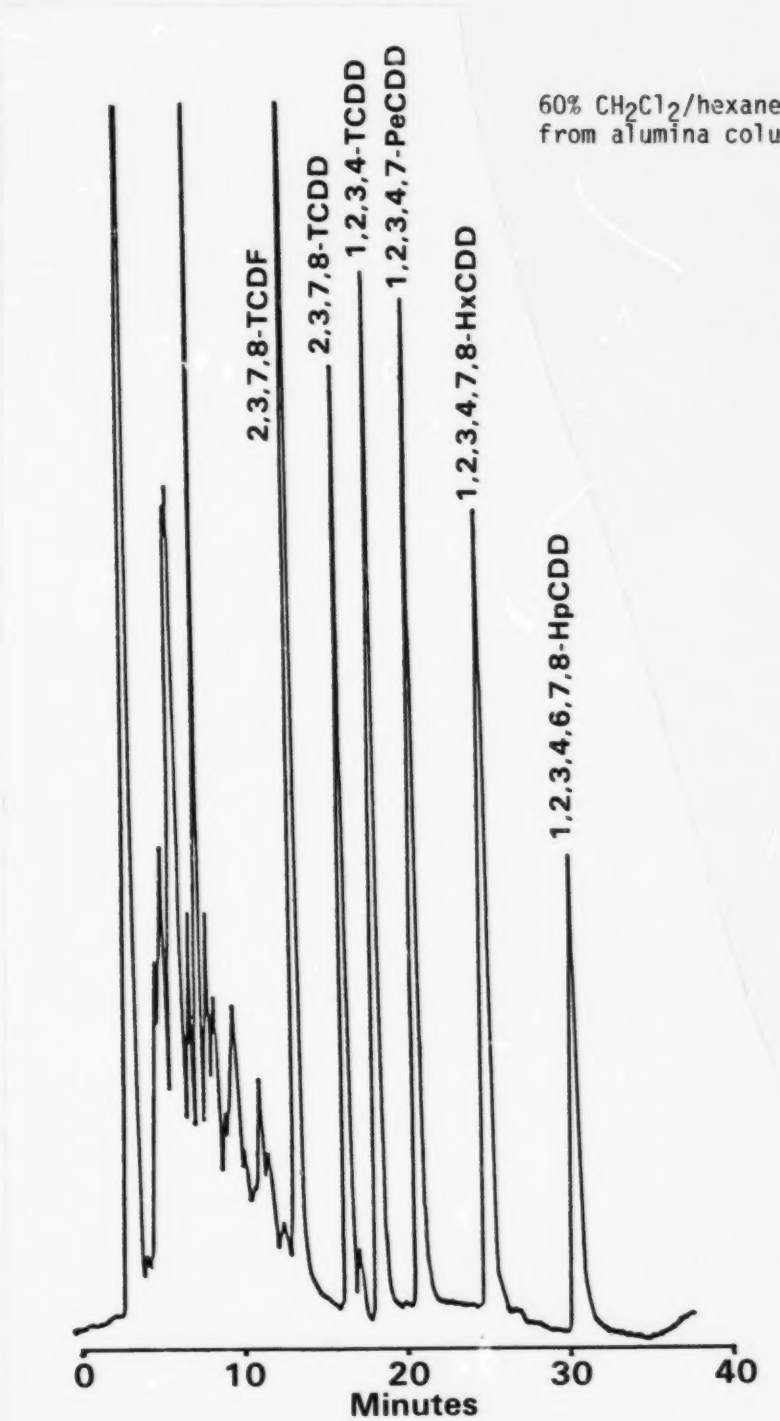

Figure 3. HPLC analysis of analyte standard mixture spiked with interference mixture.

SECTION 6

ELABORATION OF HPLC CLEANUP PROCEDURE

Since the method as published in the Federal Register provided little experimental detail regarding HPLC cleanup, a literature search was conducted to identify appropriate HPLC reverse phase operating parameters for cleanup of dioxin extracts. Two problems to be solved were: (1) to select a suitable mobile solvent phase that would be safe to work with as well as provide adequate separation for the compounds of interest, and (2) to find a fast but effective procedure to concentrate the effluent fraction as obtained from the HPLC.

Acetonitrile and/or methanol singly or mixed with 5-10 percent water were possible mobile phases. Acetonitrile possesses the drawback of a marginally high boiling point (81.6°C). Water was also eliminated because of potential problems at the evaporation step of the method. It was found when working with different solvent combinations that pure methanol performed satisfactorily as the mobile phase and produced a retention time of 16.6 minutes for 2,3,7,8-TCDD. Interferences commonly associated with 2,3,7,8-TCDD were also separated (Table 10 and Figures 1 through 3).

Evaporating the methanol effluent fraction using a gentle stream of pre-purified nitrogen and a 55°C sand bath proved to be very time consuming. Further investigation showed that concentrating this fraction to near dryness using a 2-ball micro-Snyder column and a 90°C water bath required less than 10 minutes. This more efficient extract concentration procedure was included in the revised method.

Initial recovery data indicated that very little loss of 2,3,7,8-TCDD occurred during the solvent exchange into methanol prior to HPLC injection. Recoveries of around 85 percent for 2,3,7,8-TCDD were attained for the HPLC procedure recommended for inclusion in the revised method. Further studies indicated that the major source for loss of 2,3,7,8-TCDD was the transfer step. Because the concentrator tube contained a boiling chip, the small amount of transfer solvent used to rinse the residue from the boiling chip and the walls of the concentrator tube was inadequate. An additional 100-µL solvent rinse and re-injection resulted in an additional 5 to 20 percent recovery. With the additional rinse, the recovery of 2,3,7,8-TCDD improved to approximately 95 percent.

This HPLC procedure can be very effective in the cleanup of complex samples, however, additional studies have shown that the carbon column is preferable. The HPLC procedures have not been included in the final revised method 8280.

TABLE 10. TYPICAL HPLC RETENTION TIMES OF POTENTIAL INTERFERENCES

Compound	Amount (ng)	Retention Time (min)
Pentachlorophenol	50	3.81
2,4,6-Trichlorophenol	50	5.80
2,4,5-Trichlorophenol	100	6.30
Silvex	250	6.77
Dibenzofuran	50	8.21
p,p'-DDE	100	9.22
Aroclor 1016	100	6.91 - 9.52
Aroclor 1254	100	6.91 -10.30
Aroclor 1260	200	6.75 -15.70
2,3,7,8-TCDD	25	16.6

Conditions:

2 - 4.6-mm x 25-cm octadecylsilyl columns, 5 µm particle size.
Solvent at ambient temperature, column and detector maintained at 30°C.
Flow 1 mL/min methanol (172 atm). UV detector at 235 nm, 0.02 AUFS.
100 µL sample loop.

SECTION 7

ANALYSIS OF POTTERY CLAY SAMPLES

The unrevised method 8280 specified drying the sample. However, a change in the extraction solvent system resulted in the ability to handle wet or dry samples of soil with good results. Thus, the sample selected for analyses can be more representative of that collected (whether wet or dry) and the potentially hazardous drying step can be eliminated. The new extraction procedure improved the recovery of spiked analytes from the 37 to 55 percent range (on dry clay; none detected on wet clay samples) for the unrevised procedure to the 68 to 96 percent level (on both dry and wet clays) for the revised procedure.

A representative sample of pottery clay containing no background interferences was spiked with suitable interferences and with analytes of interest (PCDD's and TCDF) to determine method performance on a clean soil matrix. The sample was homogenized and analyzed immediately. Interferences such as Silvex, DDE, and Aroclor 1260 were used at concentrations from 10 to 200 times that of each target analyte. Experiments were performed in duplicate by each of two chemists (or teams of chemists) working independently. Recoveries of analytes from pottery clay samples using the Method 8280 are summarized in Table 11, using the HRGC/EC measurement procedure.

Performance Evaluation (PE) samples from the EPA Contract Laboratory Program (CLP) were analyzed (blind) using the revised RCRA 8280 Method; the results are shown in Table 12. These pottery clay samples were spiked with nominal levels of 1 ppb TCDD and with 10 to 50 ppb levels of chlordane, DDT, DDE, and Aroclor 1260. Acceptance windows had been determined for the analysis of these PE samples under a CLP protocol.[5] A mean concentration of 0.84 ppb with standard deviation 18 percent was calculated for 21 sample analyses (interlaboratory); a 90 percent window (i.e., 90 percent of available data excluding outliers will fall within that window) was calculated at 0.53 to 1.2 ppb. As shown in Table 12, the data gathered by revised method 8280 using HRGC/LRMS all fall within this acceptance window.

TABLE 11. ANALYTE PERCENT RECOVERIES FROM POTTERY CLAY SAMPLES (HRGC/EC)*

Analyte	Samples A	B	C	D	E	F	G	$\bar{X}$	n=7 Percent Dev.
1,3,6,9-TCDD**	66.1	48.6	63.8	48.1	53.3	54.0	40.1	53.4	9.11
1,3,7,9-TCDD**	100.7	94.7	97.0	92.6	96.8	101.4	86.1	95.6	5.21
1,2,7,8-TCDF	86.8	90.7	94.7	94.7	99.0	96.8	95.1	94.0	4.04
1,3,7,8-TCDD	85.6	80.2	90.8	89.1	96.2	94.9	93.2	90.0	5.62
1,2,7,8-TCDD	87.8	80.8	91.9	91.8	99.1	98.7	91.8	91.7	6.29
1,2,8,9-TCDD	86.5	80.5	91.5	92.3	100.0	98.7	92.7	91.7	6.72
1,2,3,7,8-PeCDD	87.6	80.6	89.4	95.9	103.4	100.7	95.6	93.3	7.93
1,2,3,4,7-PeCDD	88.2	81.4	88.2	97.8	102.6	105.6	96.6	94.3	8.70
1,2,3,7,8-PeCDF	84.6	81.4	89.6	93.7	92.7	93.0	93.0	89.7	4.86
1,2,3,4,7,8-HxCDF	81.7	80.0	85.4	94.2	89.9	92.9	90.5	87.8	5.51
1,2,3,4,7,8-HxCDD	82.0	79.6	83.1	97.0	93.9	93.7	93.8	89.0	7.13
1,2,3,4,6,7,8-HpCDD	72.1	77.7	81.4	105.8	96.3	84.0	99.4	88.1	12.48
OCDF	74.2	79.3	73.0	102.2	83.2	85.3	83.3	82.9	9.70
$^{13}C_{12}$-2,3,7,8-TCDD	82.6	81.8	90.8	90.5	96.8	98.0	91.0	90.2	6.24

*Spikes at 50 ng each component (50 pg/µL in extract).
Analyses using revised Method 8280 procedures.
**Tentative isomer identification.

TABLE 12. ANALYSIS OF PERFORMANCE EVALUATION SAMPLES OBTAINED FROM CONTRACT LABORATORY PROGRAM, USING REVISED RCRA METHOD 8280

Sample ID	Nominal Concentration 2,3,7,8-TCDD	Concentration Found	$^{13}C_{12}$-2,3,7,8-TCDD Recovery
PE-1	1 ppb	1.00 ppb	62%
PE-2	1 ppb	0.81 ppb	72%
PE-3	1 ppb	1.13 ppb	90%
PE-4	1 ppb	0.94 ppb	74%

SECTION 8

ANALYSIS OF NATIVE MISSOURI SOIL SAMPLES

Native Missouri soil samples, environmentally contaminated with 2,3,7,8-TCDD and interferences such as PCB's, were obtained from the Contract Laboratory Program. These samples were thoroughly blended ("homogenized") and aliquots of 20 g each were prepared and bottled. The mean TCDD concentration of this soil reference material was determined to be 383 ppb (by an Interlaboratory study under the EPA Contract Laboratory Program). Upon analysis of this material in duplicate, the revised RCRA 8280 Method provided results of 370 and 377 ppb. Aliquots of this soil were spiked with other dioxin and dibenzofuran analytes, and percent recoveries were determined. Results of these studies are summarized in tables of accuracy and precision data included in the revised method, Appendix A.

SECTION 9

ANALYSIS OF FLY ASH SAMPLES

Municipal incinerator fly ash material was obtained in order to provide an environmental carbonaceous type matrix for testing. A partial, major component characterization of this material was performed previously (see Appendix B). This type of sample historically has required toluene or benzene extraction with Soxhlet apparatus to remove the absorbed dioxins and dibenzofurans. These analytes are often found in such samples at high ppt to low ppb levels.[6] Therefore, it was decided to spike such a sample with $^{13}C_{12}$-2,3,7,8-TCDD and to analyze by revised method 8280. Results of HRGC/MS analysis indicated the presence of numerous "native" PCDD's and PCDF's in addition to a variety of other compounds at higher levels. Figure 4 shows the portion of the mass chromatograms containing the TCDD's and TCDF's in a fly ash sample. Recovery of the carbon-13 labeled 2,3,7,8-TCDD (spiked into the sample at a concentration of 500 pg/g) was 89 percent, using toluene/Soxhlet/revised method 8280. Estimated concentrations of environmentally incorporated dioxins and dibenzofurans in the fly ash are shown in Tables 3 and 4 of Appendix A. Note that for this sample, the RCRA published extraction method (toluene/Soxhlet) was used; the revised alumina cleanup procedure was followed, and HRGC/MS was performed with the quantitation ions specified in the revised method.

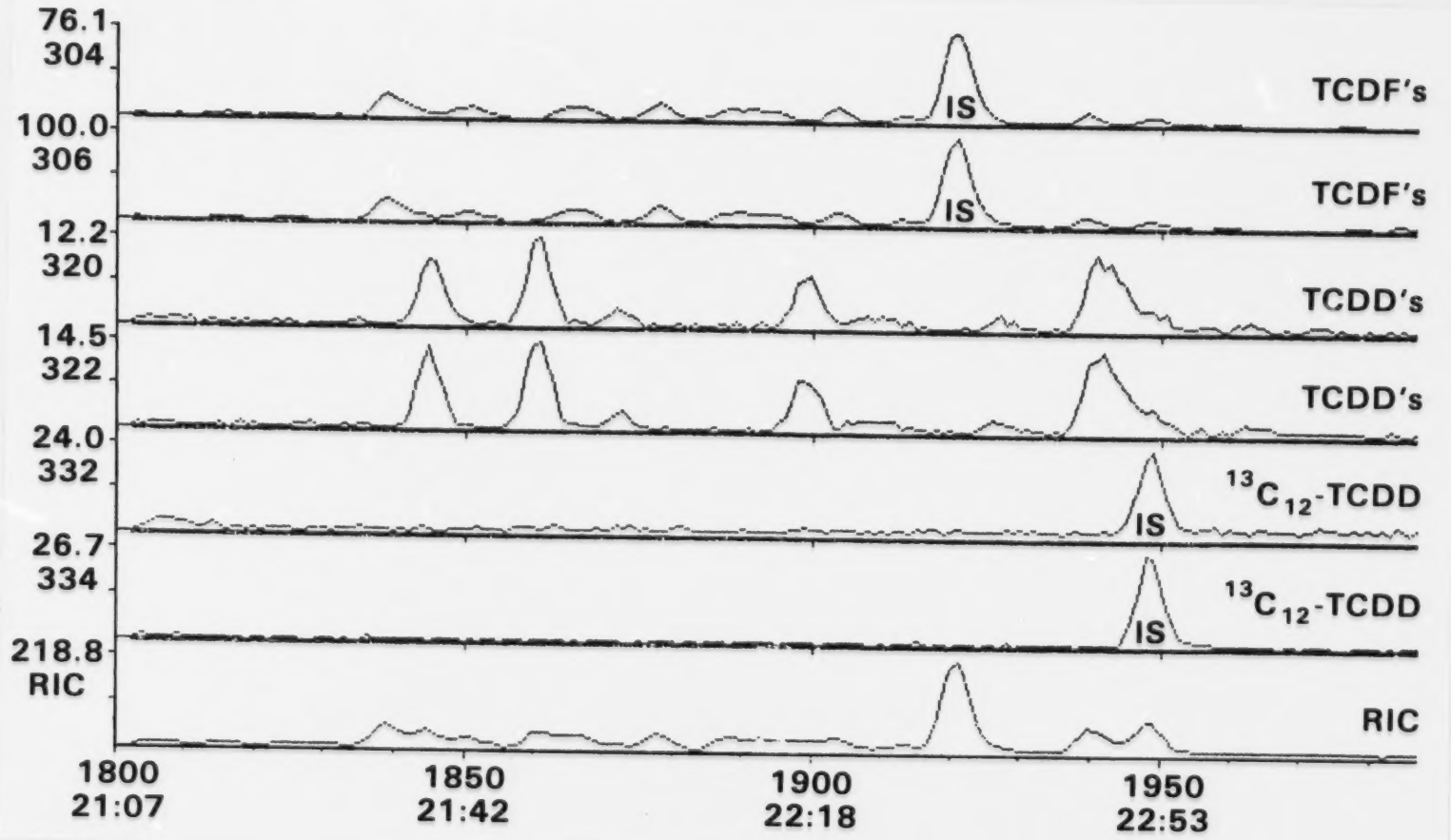

Figure 4. HRGC/MS detection of TCDD's and TCDF's in fly ash sample.

*Conditions: 10 g sample extracted and cleaned up with alumina, final volume 1 mL. Spiked with 500 pg/mL 2,3,7,8-TCDF and 500 pg/µl $^{13}C_{12}$-2,3,7,8-TCDD. Chromatographed on DB-5® (J and W Scientific, Incorporated) 170°C, 10 minutes; to 280°C at 8°/minute; hold 30 minutes at 280°C.

SECTION 10

ANALYSIS OF CHLOROPHENOL STILL BOTTOM SAMPLES

A still bottom sample from a chlorophenol production process was obtained from the EPA. The sample had been characterized by a Contract Laboratory, which reported detectable concentrations of some PCDD's and PCDF's (see Table 13). Historically, these samples have been most difficult to analyze for dioxins and dibenzofurans. Due to the presence of massive amounts of analytical interferences, poor reproducibility, low recovery of spike PCDD's and PCDF's, and relatively poor detection limits are common.[7] Nonetheless, this challenging sample represents a sample type likely to be encountered from a RCRA site. Full-scan HRGC/LRMS using a 30 m DB-5 column was performed for characterization. Through this work and later MID HRGC/LRMS work with the CP-Sil-88 and SP-2250 columns, chlorinated phenols, diphenyl ethers, and hydroxydiphenylethers ("pre-dioxins") were found, along with the target analytes. Apparently co-elution is common on all GC columns tested for dioxins, dibenzofurans, and diphenyl ethers, complicating the mass spectral analysis. Careful interpretation of spectra and retention times of standards is necessary to avoid misidentifying diphenyl ethers, benzylphenyl ethers, or hydroxydiphenylethers having similar m/z ion clusters as target PCDD's or PCDF's.

Because of the very limited success of the revised RCRA method 8280 towards analysis of this sample, additional cleanup, using a silica Spherisorb/PX-21 carbon column was incorporated into the cleanup procedure. This step has been reported by Mitchum;[8] a similar procedure has been applied by Stalling.[9] With this cleanup, good recoveries and precision were obtained as shown in Tables 3 and 4 of Appendix A. The details of the carbon column cleanup are found in Section 11.6 of the revised method.

TABLE 13. DIRECTED ANALYSES SUMMARY: 2,4-D AND 2,4-DIBE HERBICIDE DISTILLATION STILL BOTTOMS

Herbicide 2,4-Dichlorophenoxy Acetic Acid (2,4-D) and 2,4-D Isobutyl Ester (2,4-D-IBE)	
Sample	
Waste Stream No.	I11
Sample Codes	ARB 12-14-04
Description	Distillation Bottoms (tar) from DCP production
Directed Analyses	
Polychlorodibenzodioxins, µg/L (kg)	
2,3,7,8-TCDD	529 µg/kg (1)
Tetrachloro's	2,300
Pentachloro's	14,000
Hexachloro's	3,700
Heptachloro's	--
Octachloro's	--
Polychlorodibenzofurans, µg/L (kg)	
2,3,7,8-TCDF	26,000 µg/kg
Tetrachloro's	96,000
Pentachloro's	350,000
Hexachloro's	590
Heptachloro's	190
Octachloro's	6
Surrogates: (percent recovery)	
2,3,7,8-TCDD-$^{13}C_{12}$	95%
Semivolatiles, mg/L (kg)	
Phenol	
2-Chlorophenol	2,900 mg/kg
2,6-Dichlorophenol	NA
2,4-Dichlorophenol	18,000
2,4,6-Trichlorophenol	145,000
2,4,5-Trichlorophenol	--
2,6-D	NA
2,4-D	NA
2,4-D-IBE	NA
Surrogates, percent recovery	
Phenol-d_5	100.4%
Naphthalene-d_8	Not added
9-Phenylanthracene	85.2

NA - Not analyzed (1) Concentration level is for two tetrachlorodibenzo-p-dioxin isomers, one of which is the 2,3,7,8-TCDD isomer.
-- Not detected.

SECTION 11

ANALYSIS OF SLUDGE SAMPLES

A sludge sample was obtained from the EPA. The sludge represents a sample from a cooling tower that receives both creosote and pentachlorophenolic wastewaters. This sample contained a high percentage of water (76%) and rivaled the chlorophenol still bottom sample in complexity of the organic components. The water was removed by azeotropic distillation with toluene and the toluene extract was used for analysis of the PCDD's and PCDF's present. This extract was cleaned up using the revised RCRA Method 8280 procedure. This procedure included the use of a silica Spherisorb/PX-21 carbon column. The mass chromatograms before and after the silica Spherisorb/PX-21 charcoal column cleanup are shown in Figures 5 and 6. The major interferences elute in the same region as the TCDD's and TCDF's and are greatly reduced by the silica Spherisorb/PX-21 procedure. Recoveries and precision obtained are shown in Tables 3 and 4 in the revised method, Appendix A.

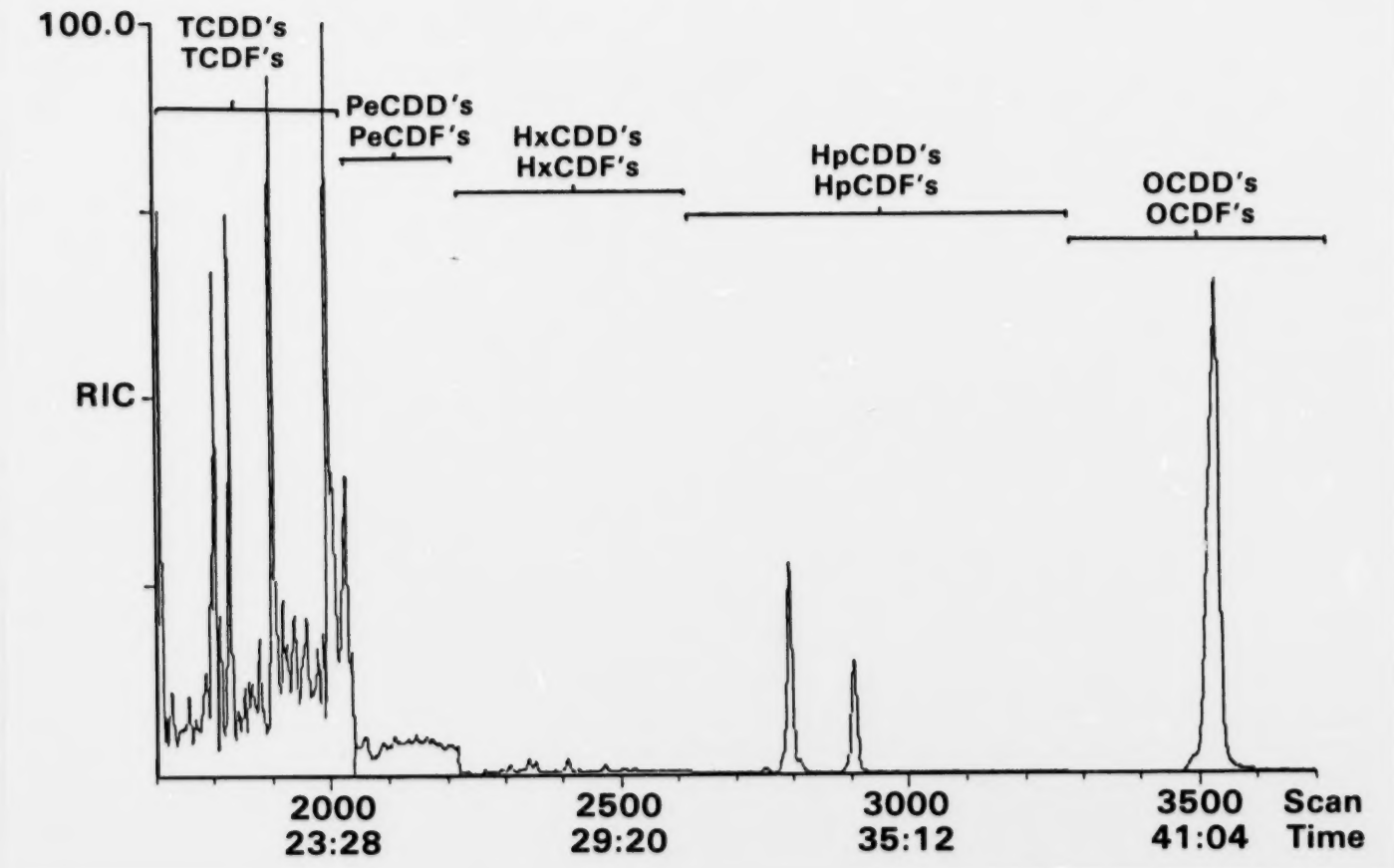

Figure 5. Mass chromatogram of sludge sample prior to silica Spherisorb/PX-21 charcoal column cleanup.

Conditions: 30 m DB-5® column (J and W Scientific, Incorporated), 170°C, 10 minutes; 170°C to 280°C at 8°/minute; hold 30 minutes at 280°C.

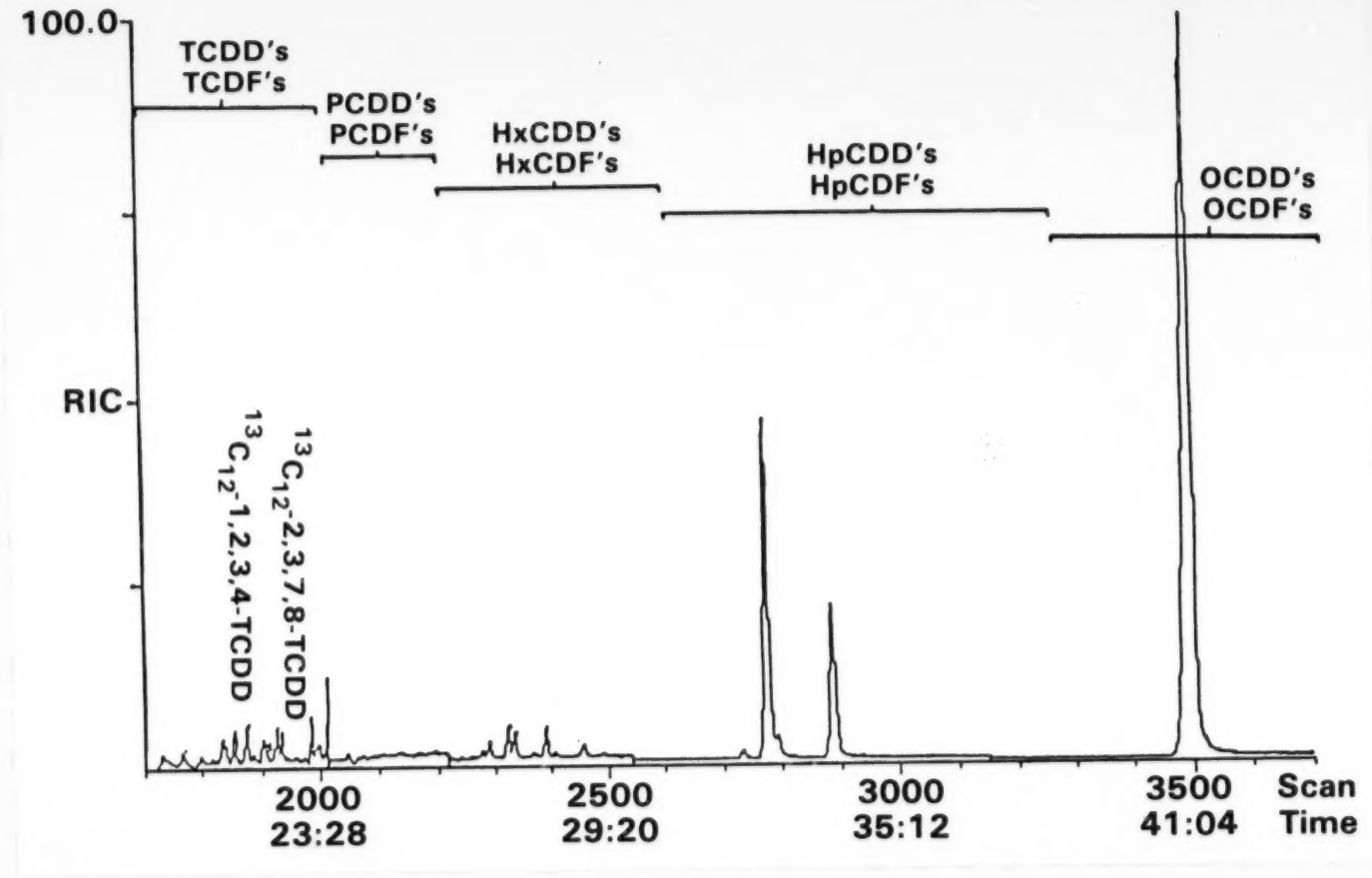

Figure 6. Mass chromatogram of sludge samples after silica Spherisorb/PX-21 charcoal column cleanup.

Conditions: 30 m DB-5® column (J and W Scientific, Incorporated), 170°C, 10 minutes; 170°C to 280°C at 8°/minute; hold 30 minutes at 280°C. Carbon-13 standards at 500 pg/µL.

SECTION 12

RATIONALE FOR PROPOSED METHOD MODIFICATIONS

The RCRA method with revisions was subjected to performance tests including (1) analysis of reference materials containing 2,3,7,8-TCDD and interferences and (2) precision and accuracy determinations on samples having known composition obtained by spiking the sample matrix. The revised method is provided in Appendix A. Rationale for each change in the method as published in the Federal Register, April 4, 1983, is presented below, section by section:

4.3.2 Fused silica capillary columns are recommended as being chromatographically equivalent to glass and easier to work with; furthermore, they can be threaded directly into the mass spectrometer source for improved sensitivity of detection. As shown in Table 1 of the revised method, four columns were evaluated using a commercially available mixture containing 1,2,3,4-TCDD, 1,2,3,4,7-PeCDD, 1,2,3,4,7,8-HxCDD, and 1,2,3,4,6,7,8-HpCDD and 2,3,7,8-TCDF. Retention times greater than about 40 to 50 minutes were considered impractical although some analytes were measured at greater retention times for comparison purposes. Both CP-Sil-88 and SP-2250 gave reasonable separation of 2,3,7,8-TCDD from the other TCDD's tested. Separations of 2,3,7,8-TCDD from the closest eluting isomer using the EPA Contract Laboratory Program GC Column Performance Check Mixture (containing seven TCDDs) were as follows: 21 percent valley on 30 m SP-2250; 16 percent valley on 50 m CP-Sil-88; 30 percent valley on 30 m DB-225; 64 percent valley on 30 m DB-5 column. Hence, separation of 2,3,7,8-TCDD from other TCDD's was best on CP-Sil-88 and poorest on 30 m DB-5. However, separation on all four columns was adequate to observe whether any close-eluting isomers (to 2,3,7,8-TCDD) were present in a given sample. Column cost is approximately proportional to length, and nonbonded phases are less durable than bonded phases such as DB-5 or DB-225. On some types of interferences, less polar columns such as DB-5 may give better separation of interferences from the analytes of interest (PCDD's and PCDF's). Temperature programs developed by this laboratory with each type of GC column are shown in Table 1.

4.3.3 The MS system should be capable of monitoring eight ions simultaneously (see Section 10.4). Sensitivity of quadrupole low-resolution systems is consistent with the revised specification of 5:1 signal to noise on 0.15 ng of native TCDD; the original specification of .015 ng of $^{37}Cl_4$-TCDD is beyond the sensitivity capabilities of many systems, particularly in EI mode and on a routine basis. Monitoring M/z 320 (or 322) is correct for native TCDD; 328 would be correct for $^{37}Cl_4$-TCDD.

4.3.4 Directly interfacing the column into the MS source is preferable and consistent with other EPA activities relating to dioxin analysis.

4.19 The added carbon column is described.

5.1 Two percent is a typographical error; 20 percent is correct.

5.3 Chemicals added reflect experience of dioxin analytical laboratories that isooctane and toluene can be suitable replacements for tridecane (or tetradecane) and benzene, respectively. [6,7]

5.5 Per experience of this laboratory, as discussed in Section 5 of this report, Woelm Super 1 alumina is specified in the revised method.

6.1 Elution patterns/retention times on "open" alumina columns and carbon columns should be verified. It is a worthwhile quality assurance measure to check the 8 percent methylene chloride/hexane fraction to ensure no analytes are lost in that fraction.

6.2 Use of $^{13}C_{12}$-TCDD labeled standards as stated is due to availability and cost.

6.3 Again, the isotopic label is changed to carbon. This change reflects availability and cost of these labeled PCDD and PCDF standards. Use of 0.15 ng native TCDD, monitored at m/z 320, reflects reasonable sensitivity requirements for quadrupole GC/MS systems. It is considered worthwhile to check GC column performance daily, because most columns that have been used for these types of analytes are subject to rapid performance degradation. Analyses conducted under the EPA-CLP have demonstrated this problem, even on relatively simple soil samples.

7.2 For some matrices/samples of interest, precision and accuracy will not be known in advance, so "determine" is more appropriate than "validate." Incorporation of field blanks into the quality assurance "package" is a standard procedure.

8.2 The sentence on sample preservation is removed. Preservation is generally considered unnecessary for these types of samples because the analytes are exceptionally stable.

9.0 Procedures are added for representative samples. The revised extraction procedure eliminates the need for drying the sample. Thus, a more representative aliquot of the total sample may be analyzed and analysis time is reduced. Dust and sample handling are reduced. Samples may be dried if analytical results based on dry sample weight are desired.

9.7 through 9.8 Method performance data are included in this report for the Method 8280 specified Woelm basic alumina and for the revised procedure's Woelm Super 1 neutral alumina. The Super 1 alumina avoids exposure of the sample to basic material, performs at least as well as the basic alumina on the separation of interferences, and requires no activation step (and concomitant possibility of contamination).

9.9 The added procedures for the carbon column cleanup are described.

10.3.3 This requirement is considered essential.[10] Diphenylether interferences are known to coelute with dibenzofuran analytes, the ethers fragment in the mass spectrometer to yield $(M-Cl_2)+$ ions with the same exact masses as chlorinated dibenzofurans. Differentiation with GC/MS analysis is, therefore, possible only from retention time and by monitoring the chlorinated diphenylether molecular ion m/z value.

10.4 For proper quality assurance, use of the monitoring ions shown in this section is important. This decision is consistent with other EPA dioxin monitoring efforts.

10.5 Another technique that has been shown (under EPA Special Analytical Services CLP efforts) to provide satisfactory results when interferences are present is HRGC/MS/MS. This technique could be included as an alternate measurement technique.

11.1 Quantitation is based on the internal standard added to the sample before extraction.

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APPENDIX A

RCRA METHOD 8280 WITH REVISIONS BASED ON SINGLE-LABORATORY TESTING:
METHOD OF ANALYSIS FOR CHLORINATED DIBENZO-P-DIOXINS
AND DIBENZOFURANS

Method 8280

1. Scope and Application

[1]This method is appropriate for the analysis of tetra-, penta-, hexa, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans.

[2]Analytical protocol for determination of TCDD's in phenolic chemical wastes and soil samples obtained from the proximity of chemical dumps. T. O. Tiernan and M. Taylor. Brehm Laboratory. Wright State University. Dayton, Ohio 45435.

[3]Analytical protocol for determination for chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans in river water. T. O. Tiernan and M. Taylor. Brehm Laboratory. Wright State University. Dayton, Ohio 45435.

1.1 This method allows for the determination of chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans in chemical wastes including still bottoms, filter aids, sludges, spent carbon, reactor residues, and in soils.

1.2 The sensitivity of this method is dependent upon the level of interferences.

1.3 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.4 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. Generators of 1 Kg or more of dioxin wastes must register as a generator. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in EPA Test Method 613.

2. Summary of the Method

2.1 This method is an extraction, cleanup procedure and high resolution capillary column gas chromatography-low resolution mass spectrometry method, using and internal standard techniques, which allow for the measurement of PCDD's and PCDF's in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination. The analysis flow chart, is shown in Figure 1.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Solvents distilled in all-glass systems are required.

3.2 Interferences co-extracted from the samples will vary considerably from source to source, depending upon the industrial process being sampled. PCDDs and PCDFs are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of analytes must be verified using standards. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches such as HPLC, to achieve the detection levels stated in Table 6.

3.3 Resolution of the 2,3,7,8-TCDD isomer from other closely eluting TCDDs is used to establish column performance criteria. High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers in a complex mixture.

4. Apparatus and Materials

4.1 Sampling equipment for discrete or composite sampling.

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for the Teflon if the sample is not corrosive.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control ($\pm 2^{\circ}C$). The bath should be used in a hood.

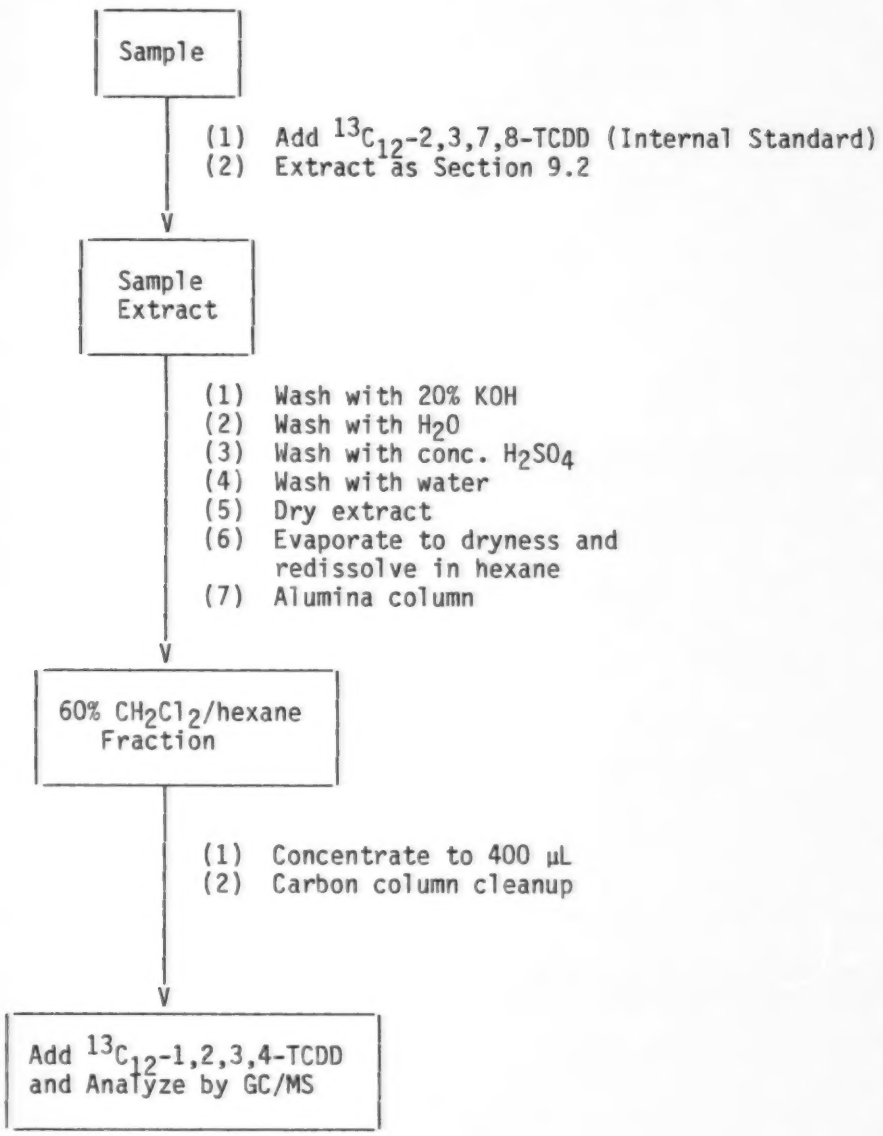
Sample
(1) Add $^{13}C_{12}$-2,3,7,8-TCDD (Internal Standard)
(2) Extract as Section 9.2
Sample Extract
(1) Wash with 20% KOH
(2) Wash with H_2O
(3) Wash with conc. H_2SO_4
(4) Wash with water
(5) Dry extract
(6) Evaporate to dryness and redissolve in hexane
(7) Alumina column
60% CH_2Cl_2/hexane Fraction
(1) Concentrate to 400 µL
(2) Carbon column cleanup
Add $^{13}C_{12}$-1,2,3,4-TCDD and Analyze by GC/MS

Figure 1. Revised Method 8280 analysis flow chart.

4.3 Gas chromatograph/mass spectrometer data system.

4.3.1 Gas chromatograph: An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, four columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 1,2,3,4,7-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50 m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) 30 m DB-5 programmed 170° for 10 minutes, then 170°-280° at 8°/minute, hold at 280°C for 30 minutes; (c) 30 m SP-2250 programmed 70°-320° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) provide separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged, and may provide better separation from certain classes of interferants.

4.3.3 Mass spectrometer: Capable of scanning from 45 to 450 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. The system must also be capable of selected ion monitoring (SIM) for at least 8 ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms. Selected ion monitoring is verified by injecting 0.15 ng of native TCDD to give a minimum signal-to-noise ratio of 5 to 1 at mass 320.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points for each compound of interest at concentration monitored and achieves acceptable tuning performance criteria (see Sections 6.1-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended.

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be able to integrate the abundance, in any EICP, between specified time or scan number limits.

4.3.6 High Performance Liquid Chromatography: HPLC pump with loop valve injector.

4.4 Apparatus Pipettes-Disposable, Pasteur, 150 mm long x 5 mm ID (Fisher Scientific Company, No. 13-678-6A or equivalent).

4.5 Amber glass bottle (500 mL, Teflon-lined screw cap).

4.6 Reacti-vial 1 mL, amber glass (silanized) (Pierce Chemical Company).

4.7 500 mL Erlenmeyer flask (American Scientific Products cat No. f4295-500f0) fitted with Teflon stoppers (ASP No. s9058-8 or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049 or equivalent).

4.9 125 mL and 2 L Separatory Funnels (Fisher (10-437-5b or equivalent).

4.10 500 mL Kuderna-Danish fitted with a 10 mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02 or equivalent).

4.11 Teflon boiling chips (Berghof American No. 15021-450 or equivalent). Wash with hexane prior to use.

4.12 300 mm x 10.5 mm glass chromatographic column fitted with Teflon stop-cock.

4.13 15 mL conical concentrator tubes (Kontes No. K-288250 or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20 or equivalent).

4.15 2-Ball micro-Snyder columns (Ace Glass No. 6709-24 or equivalent).

4.16 Nitrogen evaporator (N-Evap No. 1156 or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.17 Microflex conical vials (Kontes K-749000 or equivalent).

4.18 Filter paper (Whatman No.54 or equivalent).

4.19 Carbon Column: An HPLC column (4.6 mm x 7 cm, stainless steel), prepared by mixing 5 percent (by weight) active carbon PX-21 (Amoco Research Corporation, Chicago, Illinois, or the equivalent active carbon AX-21, washed with methanol and dried in vacuo at 110°C, Anderson Development Co., Adrian, Michigan) and 10 µm silica (Spherisorb S 10 W from Phase Separations, Inc., Norwalk, Connecticut). The material must be stirred and sieved through a 40 µm screen to remove any clumps.4/

4.20 Dean-Stark trap, 10 mL with T joints, condenser and 125 mL flask.

4/ - The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5. Reagents

5.1 Potassium hydroxide-(ACS), 20 percent (w/v) in distilled water.

5.2 Sulfuric acid-(ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tetradecane, isooctane, toluene. Distilled in glass.

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions are stored in the dark at 4°C, and checked frequently for signs of degradation or evaporation, especially just prior to the preparation of working standards.

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store at room temperature in a desiccator with $CaSO_4$ drying agent. Oven drying at 600°C overnight is acceptable, but alumina so processed should be checked for contamination by solvent rinsing and GC/ECD analysis.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade). Extracted overnight with hexane using a Soxhlet extraction apparatus and dried at 100°C.

6. Calibration

6.1 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from reagents. Both open column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

6.2 Prepare multi-level calibration standards keeping the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) and the internal standard 5/ ($^{13}C_{12}$-2,3,7,8-TCDD) at fixed concentrations of 500 ng/mL. Recommended concentration levels for standard analytes are 200, 500, 1000, 2000, and 5000 ng/mL. Calculation of response factors is described in Section 11.1. Standards must be analyzed using the same solvent as used in the final extract, toluene is recommended. A wider calibration range is useful provided it can be described within the linear range of the method.

5/ - $^{13}C_{12}$-labeled TCDD is available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper standardization requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution mass spectral analysis.

6.3 Establish operating parameters for the GC/MS system as indicated in Section 10.1 of this method. The instrument should be tuned as described in Table 2 by the use of decafluorotriphenyl phosphine (DFTPP). By injecting calibration standards, establish the standard response factors vs. $^{13}C_{12}$-2,3,7,8-TCDD (PCDF response factors are established, vs. $^{13}C_{12}$-TCDF if this standard is used). An adequate detection limit should be verified by injecting 0.15 ng of $^{13}C_{12}$-2,3,7,8-TCDD which should give a minimum signal to a noise ratio of 5 to 1 at mass 330. GC column performance should be checked for resolution and peak shape daily using a mixed standard such as the GC column performance check mixture described in Section 4.3.2.

7. Quality Control

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted, or there is a change in reagents, a method blank shall be processed as a safeguard against laboratory contamination.

7.2 Standard quality assurance practices must be used with this method. Field replicates must be collected to validate the precision of the sampling technique. Laboratory replicates must be analyzed to determine the precision of the analysis. Fortified samples must be analyzed to establish the accuracy of the analysis. Field blanks must be collected to verify that sample collection processes are free from cross-contamination.

8. Sample Collection, Preservation, and Handling

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices should be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing and other potential sources of contamination.

8.2 All samples must be stored at 4°C, extracted within 7 days and completely analyzed within 30 days of collection.

9. Extraction and Cleanup Procedures

9.1 Internal standard addition. Use an aliquot of 0.1-10 g sample (typical sample size requirements for each type of matrix is provided in Section 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, which is employed as an internal standard. All samples should be spiked with the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD, to give an approximate concentration of 500 pg/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 µL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, at 100% recovery.

9.2 Extraction

9.2.1 Sludge. Extract the sludge samples by refluxing a 2 g sample with

50 mL of toluene in a 125 mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene solution through Whatman No. 54 filter paper (or equivalent) into a 100 mL round bottom flask. Concentrate the extract to just dryness using a rotary evaporator at 50°C. Proceed with step 9.2.4.

9.2.2 Still bottom. Extract the still bottom sample by mixing 100 mg of sample with 10 mL of toluene and filtering the solution through Whatman No. 54 filter paper (or equivalent) into a 50 mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to just dryness using a rotary evaporator at 50°C. Proceed with step 9.2.4.

9.2.3 Fly ash. Extract the fly ash sample by placing 10 g of sample and 10 g of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with toluene and extract for 16 hours using a three cycle/hour schedule. Cool and filter the toluene extract through Whatman No. 54 filter paper (or equivalent) into a 500 mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution just to dryness using a rotary evaporator at 50°C. Proceed with step 9.2.4.

9.2.4 Transfer the residue to a 125 mL separatory funnel using 15 mL of hexane. Rinse the flask with 2-5 mL aliquots of hexane and add the rinses to the funnel. Shake 2 minutes with 50 mL of 5% NaCl solution, discard the aqueous layer and proceed with step 9.3.

9.2.5 Soil. Extract soil samples by placing 10 grams of sample and 10 grams of anydrous sodium sulfate in a 500 mL Erlenmeyer flask fitted with a Teflon stopper. Add 70 mL of petroleum ether and 30 mL for methanol, in that order, to the Erlenmeyer flask. Shake on a wrist-action shaker for two hours. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Section 9.2.5 through a glass funnel fitted with filter paper (Whatman No. 54 or equivalent) and filled with anhydrous sodium sulfate into a 500 mL Kuderna-Danish (KD) concentrator fitted with a 10 mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Wash the sodium sulfate on the funnel with two 5 mL portions of petroleum ether.

9.2.5.2 Add a Teflon boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C steam bath to an apparent volume of 10 mL. Remove the apparatus from the steam bath and allow it to cool for 5 minutes.

9.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a steam bath to an apparent volume of 10 mL. Remove the apparatus from the steam bath and allow to cool for 5 minutes.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two, 1 mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125 mL separatory funnel. Rinse the KD with two additional five mL portions of hexane, combine. Proceed with step 9.3.

9.2.6 Aqueous samples. Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1 L) into a 2-L separatory funnel. Note: A continuous liquid-liquid extractor may be used in place of a separatory funnel.

9.2.6.1 Add 60 mL methlylene chloride to the sample bottle, seal and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract tne sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface beteen layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500 mL Kuderna-Danish concentrator (mounted with a 10 mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column and concentrate the extract until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, add 50 mL hexane, reattach the Snyder column and concentrate to approximately 5 mL. Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Step 9.3

9.3 Partition the solvent against 40 mL of 20 percent (w/w) potassium hydroxide. Agitate for two minutes. Remove and discard the aqueous layer (bottom).

9.4 Partition the solvent against 40 mL of distilled water. Agitate for two minutes. Remove and discard aqueous layer (bottom).

9.5 Partition the solvent against 40 mL of concentrated sulfuric acid. Agitate for two minutes. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer.

9.6 Partition the extract against 40 mL of distilled water. Agitate for two minutes. Remove and discard aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate, wash with two 5 mL portions of hexane, and concentrate the hexane solution to near dryness with a rotary evaporator (35°C water bath).

9.7 Pack a gravity column (glass 300mm x 10.5mm), fitted with a Teflon stopcock, in the following manner:

Insert a glass-wool plug into the bottom of the column. Add a 4 gram layer of sodium sulfate. Add a 3.6 gram layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored and sealed in a desiccator. Add a

4 gram layer of sodium sulfate. Elute with 20 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the effluent. Check the column for channeling. If channeling is present discard the column. Do not tap on a wetted column.

9.8 Dissolve the residue from 9.6 in 2 mL of hexane and apply the hexane solution of the sample to the top of the column. Elute with enough hexane to transfer the sample cleanly to the surface of the alumina. Discard the effluent.

9.8.1 Elute with 10 mL of 8 percent methylene chloride by volume in hexane. Check that no PCDD's or PCDF's eluted in this fraction as a quality assurance step.

9.8.2 Elute the PCDD's and PCDF's from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15 mL) concentrator tube.

9.9 Carbon column cleanup.

9.9.1 Using N_2, gently concentrate both fractions from the alumina column (Section 9.8) to about 1 mL. Wash the sides of the tube with a small volume (100-300 µL) of hexane and reconcentrate to about 1 mL. Save the 8 percent fraction for GC/MS injection to check for any bleedthrough of PCDD's and PCDF's (a quality assurance step). Evaporate the 60 percent CH_2Cl_2/hexane fraction to about 400 µL and prepare for transfer to a HPLC injector loop (1.0 mL) for carbon column cleanup. Rinse the centrifuge tube with 500 µL hexane, and add both fractions to HPLC injector loop.

9.9.2 Elute the column at 2 mL/minute, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard effluent. Next elute the column with 10 mL of CH_2Cl_2/MeOH/Benzene 70:20:5 (v/v). Discard effluent. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is cleaned by pumping an additional 30 mL methanol followed by 40 mL of toluene in the back flush position. After returning the column to the original position, 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through the column to reequilibriate it in preparation for the next sample. The column must be checked for bleed following the analysis of high level samples (>500 ppb) and replaced as needed.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0 mL reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2.

9.10 Approximately 1 hour before HRGC/LRMS analysis, add the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD, to give a concentration of 500 ng/mL) to the residue in the reacti-vial. Add an appropriate quantity of toluene. The final volume should be 100 µL for soil samples, 500 µL for sludge and still bottom samples and 1 mL for the fly ash samples the correct volume will depend on the relative concentration of target analytes. Gently swirl the solvent on the lower portion of the vessel to ensure dissolution of the PCDD's and PCDF's. Inject an appropriate aliquot (1 or 2 µL) of the sample into the GC/MS instrument, using a syringe.

10. GC/MS Analysis

10.1 When toluene is employed as the final solvent use of a bonded phase column from Section 4.3.2 is recommended. Solvent exchange into isooctance or tridecane is required for other liquid phases on nonbonded columns.

10.2 Calculate response factors for standards relative to the internal standard $^{13}C_{12}$-2,3,7,8-TCDD (see Section 11). Add the recovery standard to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that of the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring using ions listed in Table 3. Proof of the presence of PCDD or PCDF exists if the following conditions are met:

10.3.1 The relative retention time of the peak in the sample must match that in the standard, within the performance specifications of the analytical system (less than 0.01 units variation in relative retention time is expected).

10.3.2 The isotopic ratio of ions within the parent cluster must agree within 10 percent of the theoretical value as confirmed by the analysis of standards.

10.3.3 For confirmation of a PCDF, molecular ion response (m/z 374, 376, for example) for diphenyl ethers must be absent at the retention time.

10.4 Quantitate the PCDD and PCDF peaks from the response relative to the $^{13}C_{12}$-2,3,7,8-TCDD internal standard. Recovery of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD vs. the recovery standard $^{13}C_{12}$-1,2,3,4-TCDD must be greater than 50 percent. Samples with recoveries of less than 50 percent must be reanalyzed. It is recommended that the GC/MS run be divided into 4 scan monitoring sections monitoring, respectively: (1) 241, 257, 304, 306, 320, 322, 332, 334 (TCDD's, TCDF's + $^{13}C_{12}$ internal and recovery standards); (2) 275, 291, 338, 340, 342, 354, 356, 358 (PeCDD's and PeCDF's); (3) 311, 327, 372, 374, 376, 388, 390, 392 (HxCDD's and HxCDF's); (4) 345, 361, 406, 408, 410, 422, 424, 426 (HpCDD's and HpCDF's) and (5) 379, 395, 440, 442, 444, 456, 458, 460 (OCDD and OCDF). Cycle time "not to exceed" 1 second/descriptor.

10.5 Additional confirmation using isotopic ratio measurements must also be defined for each member of the homologous series.

10.6 In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

11. Calculations

11.1 Determine the concentration of individual compounds according to the formulas:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times R_f}$$

Where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of characteristic ion of the compound of interest.

A_{is} = area of characteristic ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

R_f = response factor of the characteristic ion of the compound of interest relative to the m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

Response factors are calculated using data obtained from the analysis of standards according to the formula:

$$Rf = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

C_{is} = concentration of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

C_s = concentration of the compound of interest.

Calculate recovery of the internal standard, R_{is}, $^{13}C_{12}$-2,3,7,8-TCDD, in the sample extract, using for formula:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times R_{fr} \times Q_{is}} \times 100$$

Where:

A_{rs} = Area of characteristic ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of standards according to the formula:

$$Rf_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

Where:

C_{rs} = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.2 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.3 Accuracy and Precision. Table 3 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 4 gives recovery data for the same analyses. Table 5 give the linear range and variation of response factors over the range for selected analyted standards. Table 6 gives estimated detection limits.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

Analyte	50 m CP-Sil-88	30 m DB-5	30 m SP-2250	30 m DB-225
2,3,7,8-TCDD	23.6	22.8	26.7	37.3
1,2,3,4-TCDD	24.1	22.7	26.5	37.6
1,2,3,4,7-PeCDD	30.0	25.2	28.1	NM
1,2,3,4,7,8-HxCDD	39.5	28.0	30.6	NM
1,2,3,4,6,7,8-HpCDD	57.0	34.2	33.7	NM
2,3,7,8-TCDF	25.2	22.5	26.7	42.5

* Retention time in minutes, using temperature programs shown below.

NM = not measured.

Temperature Programs:

CP-Sil-88	60°C-190°C at 20°/minute; 190°-240° at 5°/minute.
30 m DB-5	170°, 10 minutes; then at 8°/minute to 280°C, hold at 280°C 30 minutes.
SP-2250	70°-320° at 10°/minute.
DB-225	70°-230° at 10°/minute.

Column Manufacturers

CP-Sil-88	Chrompack Incorporated, Bridgewater, New Jersey
DB-5, DB-225	J and W Scientific, Incorporated, Rancho Cordova, California
SP-2250	Supelco, Incorporated, Bellefonte, Pennsylvania

TABLE 2. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60 percent of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40-60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5-9 percent of mass 198
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

J. W. Eichelberger, L. E. Harris, and W. L. Budde. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47, 995 (1975).

TABLE 3. PRECISION DATA FOR REVISED METHOD 8280

Compound	Matrix[1]	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[2]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom	487	487	4	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	fly ash	38.5	38.5	4	7.9
	still bottom	ND	2500	4	-
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	19.1	2	-
	still bottom	227	2727	2	-
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	58.4	2	-
	still bottom	ND	2500	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	16.0	4	3.5
	still bottom	422	2920	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	2.6	3	23
	still bottom	ND	2500	2	-
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-

(continued)

TABLE 3. (Continued)

Compound	Matrix	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	25.8	2	6.9
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	-
	soil	ND	25.0	4	-
	sludge[3]	8760	8780	4	-
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	7.4	3	7.6
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom[3]	25600	28100	2	-
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	24.2	4	13.5
	still bottom	ND	2500	2	-

(continued)

TABLE 3. (Continued)

Compound	Matrix	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
OCDF	clay	ND	-	-	-
	soil	ND	-	-	-
	sludge	192	317	4	3.3
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-

[1] matrix types:

clay: pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator, resource recovery ash No. 1, as described in Appendix B.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production obtained from Arthur D. Little, Inc., 1983.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only. (Carbon column not used.)

[2] ND - not detected at concentration injected (final volume 0.1 ml or greater).

[3] Estimated concentration out of calibration range of standards.

TABLE 4. RECOVERY DATA FOR REVISED METHOD 8280

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	-	-
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	-	-
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	615	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2

(continued)

TABLE 4. (Continued)

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[4]	8780	125	-
	fly ash	ND	-	-
	still bottom	ND	-	-
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25,600	2500	-

(continued)

TABLE 4. (Continued)

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	-	-
	soil	ND	-	-
	sludge	192	125	86.8
	fly ash	ND	-	-
	still bottom	ND	-	-

[1] matrix types:

clay: pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator, resource recovery ash No. 1, as described in Appendix B.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production obtained from Arthur D. Little, Inc., 1983.

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[2] Final volume of concentrate 0.1 ml or greater, ND means below quantification limit, 2 or more samples analyzed.

[3] Amount of analyte added to sample, 2 or more samples analyzed.

[4] Estimated concentration out of calibration range of standards.

TABLE 5. LINEAR RANGE AND VARIATION OF RESPONSE FACTORS

Analyte	Linear Range Tested (pg)	n**	Mean RF	%RSD
1,2,7,8-TCDF*	50-6000	8	1.634	12.0
2,3,7,8-TCDD*	50-7000	7	0.721	11.9
2,3,7,8-TCDF	300-4000	5	2.208	7.9

* Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

** Each value of n represents a different concentration level.

TABLE 6. DETECTION LIMITS (ppb) FOR RCRA METHOD 8280[1,2]

Analyte Class	Clay	Soil	Fly Ash	Still Bottom[3]	Sludge
TCDD	1.0	5.0	1.0	500	25
TCDF	0.5	2.5	0.5	250	12
PeCDD	1.5	7.5	1.5	750	38
PeCDF	1.0	5.0	1.0	500	25
HxCDD	2.0	10	2.0	1000	50
HxCDF	1.5	7.5	1.5	750	38

1 The analytes of the class indicated were not quantified below this value. The instrument detection limit (S = 3 x Noise) for 2,3,7,8-TCDD in standards is 0.5 ppb when extrapolated for a 10 g sample concentrated to 100 µL.

2 Matrix types:

Clay: Pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

Soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0. The 90 percent window was 143 to 469 ng/g.

Fly Ash: Ash from a municipal incinerator, resource recovery ash No. 1, as described in Appendix B.

Still Bottom: Distillation bottoms (tar) from 2,4-dichlorophenol production obtained from Arthur D. Little, Inc., 1983.

Sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column (carbon column not used).

3 The still bottom samples were not tested below this level due to high analyte levels found.

APPENDIX B

HOMOGENIZATION AND CHARACTERIZATION OF RESOURCE RECOVERY FLY ASH NO. 1

Experimental: Approximately 5 lb. (2100 g) of resource recovery fly ash No. 1 (RRA No. 1) was homogenized by prolonged tumbling in a rotary extractor. Next, 144 aliquots of 10 g each were placed in amber glass bottles fitted with Teflon™ lined screw caps; the aliquots were stored in a freezer. Twelve aliquots selected randomly were extracted by a Soxhlet procedure (SW 846-Method 3540) and the extracts were submitted for GC/MS analysis (SW 846-Method 8270). The same 12 extracts were also analyzed according to the IFB GC/MS protocol and the results are included in Table 1 for comparison.

Results: Table 1 shows the concentrations of the semi-volatile priority pollutants (SVPP's) in ppm determined in RRA No. 1, together with the percent recovery of surrogate spikes. Because the concentrations of several SVPP's (e.g., naphthalene, di-n-butyl phthalate, chrysene) were lower than those previously determined on 5-g aliquots of RRA No. 1 (see Table 2), a further 12 aliquots (10 g) were Soxhlet-extracted under rigorously controlled conditions for optimum extraction efficiency. The results which are shown in Table 3 were generated by taking the mean of all 12 values determined for each analyte. The results within each set of six are consistent (generally low percent RSD) and are generally consistent between the sets.

Conclusions: A total of 24 randomly selected aliquots of RRA No. 1 have been analyzed under two different GC/MS protocols (IFB; SW-846). The consisitent results obtained both between the protocols (Table 1) and between the sample sets indicate that the material is homogeneous. Inspection of Lockheed's Statistical Design for Matrix Characterization for this project indicates that a power level of 80 percent is attained for all analytes, except benzo(a)-anthracene, which has a power level of 60 percent. Because of the reproducible results obtained, RRA No. 1 is recommended as suitable for use as a stand-alone reference material.

TABLE 1. CONCENTRATION OF SEMI-VOLATILE PRIORITY POLLUTANTS IN RESOURCE RECOVERY FLY ASH NO. 1 IN PPM

Pollutant	IFB GC/MS Protocol Mean	n=12	RSD%	SW-846 GC/MS Protocol[a] Mean	n=12	RSD%
Naphthalene	4.8		8.8	4.56		7.5
Acenaphthylene	0.79		17.9	0.58		46.3
Phenanthrene[b]	23.6		13.6	20.3		5.2
Di-n-butyl phthalate	1.50		15.2	1.30		14.6
Dibenzofuran	1.52		7.9	1.46		4.2
Benzo(a)anthracene	0.88		20.8	0.92		21.2
Chyrsene	3.26		13.7	4.11		14.5
Bis(2-ethylhexyl)-phthalate	1.10		32.1	1.49		44.9
Fluoranthene[c]	30.5		10.1	31.0		6.2
Pyrene[c]	9.38		7.6	9.9		8.1
Surrogate Spikes % Recovery						
2-Fluorophenol	31.9		16.9	43.7		15.6
Phenol-d5	52.1		21.1	48.2		17.7
Pentafluorophenol	40.3		18.2	41.1		26.8
Nitrobenzene-d5	53.8		9.6	65.4		9.1
2-Fluorobiphenyl	83.2		11.0	78.7		6.2
Decafluorobiphenyl	62.9		17.5	71.5		8.0
Pyrene-d10	69.4		12.5	77.6		9.5
2-Fluoroaniline	2.98		67.1	N.D.		-

[a]Concentrated extract was diluted 1:1 with dichloromethane for analysis.

[b]Quantitation ion m/z 176 (not m/z 178) to avoid saturation.

[c]Quantitation ion m/z 200 (not m/z 202) to avoid saturation.

TABLE 2. SOXHLET EXTRACTION OF RESOURCE RECOVERY FLY ASH NUMBER 1
CONCENTRATION OF SEMI-VOLATILE PRIORITY POLLUTANTS
(ASSUMING 100% EXTRACTION EFFICIENCY) IN PPM

Pollutant	Mean	RSD% (n=5)
Naphthalene	7.5	4.7
Acenaphthylene	1.18	17.2
Phenanthrene	23.0	12.3
Di-n-butyl phthalate	5.2	33.7
Dibenzofuran	1.68	21.2
Benzo(a)anthracene	1.82	38.3
Chyrsene	6.28	17.4
Bis(2-ethylhexyl)phthalate	3.24	26.7
Fluoranthene	39.2	16.6
Pyrene	13.5	19.0
Surrogate Spikes % Recovery		
2-Fluorophenol	83.7	6.8
Phenol-d5	73.4	12.0
Pentafluorophenol	20.4	78.5
Nitrobenzene-d5	64.0	11.3
2-Fluorobiphenyl	105.0	4.0
Decafluorobiphenyl	121.6	17.5
Pyrene-d10	102.6	8.1

TABLE 3. CONCENTRATION OF SEMI-VOLATILE PRIORITY POLLUTANTS IN RESOURCE RECOVERY FLY ASH NO. 1, PPM

Pollutant	SW-846 GC/MS Protocol Mean, n=12	RSD%
Naphthalene	4.73	15.1
Acenaphthylene	0.97	17.8
Phenanthrene	18.4	10.9
Di-n-butyl phthalate	1.24	50.2
Dibenzofuran	1.46	18.6
Benzo(a)anthracene	1.28	13.9
Chyrsene	5.18	7.5
Bis(2-ethylhexyl)phthalate	1.05	21.7
Fluoranthene	32.1	25.0
Pyrene	11.3	6.9
Surrogate Spikes % Recovery		
2-Fluorophenol	50.9	24.2
Phenol-d5	62.7	11.7
Pentafluorophenol	56.2	13.1
Nitrobenzene-d5	66.1	7.0
2-Fluorobiphenyl	76.4	5.2
Decafluorobiphenyl	58.5	11.8
Pyrene-d10	90.2	7.4
2-Fluoroaniline	25.6	56.9